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Technical Advisor

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In-Situ Oxygen-Atom Erosion Study of a Polyhedral Oligomeric Silsesquioxane Polyurethane Copolymer

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ABSTRACT

The surface of a polyhedral oligomeric silsesquioxane polyurethane copolymer has been characterized in-situ using X-ray photoelectron spectroscopy before and after exposure to incremental fluences of oxygen atoms produced by a hyperthermal oxygen atom source. The data indicate that the atomic oxygen initially attacks the cyclopentyl groups that surround the polyhedral oligomeric silsesquioxane cage, resulting in the formation and desorption of CO₂ from the surface. The carbon concentration in the near surface region is reduced from 72.5 at% for the as-entered surface to 37.8 at% following 63 hrs of O-atom exposure at a flux of 10^{14} O-atoms/cm²-s. The oxygen and silicon concentrations are increased with incremental exposures to the O-atom flux. The oxygen concentration increases from 18.5 at% for the as-entered sample to 32.6 at% following the 63 hr exposure, and the silicon concentration increases from 8.1 to 11.1 at% after 63 hrs. The data reveal the formation of a silica layer on the surface which serves as a protective barrier preventing further degradation of the polymer underneath with increased exposure to the O-atom flux.

KEY WORDS: atomic oxygen, POSS, silsesquioxane, polymer, space, space materials

1. INTRODUCTION

Polymeric materials offer many advantages for Low Earth Orbit (LEO) applications, including ease of processing and reduced payload-to-orbit costs from the reduction in weight. However, over the last two decades it has been well established that polymers used in the construction of space vehicles undergo severe degradation, resulting in reduced spacecraft lifetimes. These materials degrade because spacecraft surfaces must endure high fluxes of atomic oxygen (AO), bombardment by low and high-energy charged particles, thermal cycling and the full spectrum of solar radiation. Many studies have been conducted in an effort to determine the mechanism of this degradation primarily caused by surface reactions with AO. (1-9) However, these studies have all been carried out after exposing these highly reactive surfaces to air prior to analysis, thus introducing artifacts that do not represent the true nature of space. Recent studies have shown that exposure to air chemically alters the reactive surfaces formed during AO exposure. (10,11) It is, therefore, essential that analysis of polymers exposed to AO be carried out in-situ to avoid artifacts induced by air exposure.

In this study, a solvent casted film of polyhedral oligomeric silsesquioxane (POSS)-polyurethane (PU) copolymer has been characterized in-situ using X-ray photoelectron spectroscopy (XPS) before and after incremental exposures to the flux produced by an electron stimulated desorption (ESD) atomic oxygen source. (12) POSS molecules are hybrid inorganic/organic structures synthesized from the self-condensation reactions of alkyl trichlorosilanes. Over the last seven years, Lichtenhan and coworkers have focused on incorporating POSS frameworks into traditional polymer systems via copolymerization, grafting and blending processes. (13-19) Three primary POSS-polymer architectures (bead, pendant or crosslinked) are available for use in thermoset systems or in copolymerizations, as shown in

Figure 1. Significant property enhancements have been reported for these hybrid polymers including increased use temperature, increased toughness, decreased flammability and increased oxidation resistance. These property enhancements are attributed to the nano-level interaction of the POSS framework with the polymer matrix. Traditionally, silica fillers have been used in polymer applications requiring alterations in physical and mechanical properties such as tensile strength, abrasion and fatigue resistance. In addition to numerous property enhancements, POSS polymers have lower densities (1.2 to 1.5 g/ml) than silica fillers (2.4 to 2.6 g/ml). (20,21) Unlike silica fillers, POSS frameworks can be easily functionalized for polymer compatibility without significantly affecting processing conditions. Compared to silica fillers, POSS hybrid polymers are able to impart similar property enhancements, including many not possible utilizing filler technology. Previous studies have also shown that Si-O systems exhibit a superior resistance to AO degradation, due in part to their oxophilicity and high bond strength (~ 8 eV). (22,23) However, pure siloxane systems have displayed many disadvantages for space applications, including the generation of volatile cyclic species when exposed to AO that can recondense on optical surfaces. (24) Recent testing of POSS-containing polymers has shown promising AO resistant properties. In-situ XPS analysis has revealed that, upon exposure to AO, these hybrid organic/inorganic polymers rapidly form a ceramic-like, passivating SiO_2 layer that prevents further degradation of the underlying polymer. (25,26) Similar observations are reported for the POSS-polyurethane sample examined in this study.

2. EXPERIMENTAL

2.1 O-Atom Source Characteristics

The ESD source used in this study was developed by Hoflund and Weaver (12) and is commercially available through Atom Sources, Inc. It is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high-purity, hyperthermal, AO flux with an O atom: O^+ ratio of $\sim 10^8$. These sources are superior to plasma sources in that they produce hyperthermal, ground-state O atoms and operate at UHV pressures ($\sim 10^{-9}$ torr) with negligible amounts of other species, including ions, contaminants and UV radiation. The operational concept of the hyperthermal oxygen atom generator is shown in Figure 2. Ultrahigh purity molecular O_2 dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature ($\sim 400^\circ C$) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of O atoms forming a continuous flux. Many processes have to function in series at sufficiently high rates for the system to work, including dissociative adsorption of the molecular gas on the metal surface, permeation of atoms through the membrane, and formation of the neutral flux by ESD. Some bremsstrahlung radiation is produced by the electrons striking the Ag membrane. Because the UV component is small, this radiation has only a small effect on the chemical processes occurring at the sample surface. Another potential problem is the sublimation of Ag from the membrane surface which could accumulate on the sample surface. Studies have been performed to optimize the power input to the membrane surface so that the O flux is maximized while the Ag sublimation rate is negligible. This is possible because the Ag sublimation rate decreases exponentially with temperature.

The O atoms produced by this source have been shown to be hyperthermal, but their energy distribution has not been measured. Corallo et al. (27) have measured the energy distribution of O ions emitted by ESD from a Ag (110) surface and found that this distribution has a maximum of ~ 5 eV and a full-width at half maximum of 3.6 eV. This ion energy distribution would set an upper bound for the neutral energy distribution because ESD neutrals are generally believed to be less energetic than ESD ions. This point has been discussed often in the ESD literature but not actually demonstrated. A mass spectrometer has been used to characterize the flux produced by this ESD source. The ion acceleration potential was set at 0.0 V in these studies. Since calibration studies demonstrated that the ions entering the quadrupole section had to have a minimum kinetic energy of 2.0 eV to reach the detector, the ESD neutrals have a minimum energy of 2 eV. Therefore, the hyperthermal AO produced by this ESD source have energies greater than 2 eV but less than the ion energy distribution.

2.2 Preparation of the 20 wt % POSS-Polyurethane Copolymer

Polyurethane samples were synthesized by a two-step solution reaction (Figure 3) described by Hsiao et al. (28). Diphenylmethane-4,4'-diisocyanate (MDI) and polytetramethylene glycol (PTMG) ($M_w=2000$) were mixed in a molar ratio of 2:1 and prepolymerized at 80°C for 2 hrs. The prepolymer was dissolved into anhydrous polytetrahydrofuran (PTHF). The prepolymer was then chain extended by addition of POSS-TMP diol at room temperature over 6 hrs. The mixture was cooled to 5 °C and 1,4-butanediol (BDO) added drop-wise. The system was warmed to room temperature, and after 1 hour the products were precipitated in a 1:1 methanol-water solution, separated by filtration and dried in vacuo. All the reactions were carried out under nitrogen.

2.3 Preparation of Thin Films by Solvent Casting

Thin films of the 20 wt% POSS-PU were made by solvent casting THF solutions of 5mg/mL concentration of each polymer onto 1 cm x 1 cm aluminum substrates. The films were dried at room temperature for 24 hrs. The aluminum substrates were cleaned with BoraxoTM soap and water, rinsed with deionized water, followed by ultrasonic cleaning in toluene, acetone, trichloroethylene, acetone and ethanol successively.

2.4 Surface Characterization

A solvent-casted 20 wt% POSS-PU film was wiped with isopropanol and inserted into the UHV chamber (base pressure $<10^{-10}$ torr). XPS was performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV using Mg $K\alpha$ X-rays (PHI Model 04-151 x-ray source). Data collection was accomplished using a computer interfaced, digital pulse-counting circuit (29) followed by smoothing with digital-filtering techniques (30). The sample was tilted 30 deg off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 deg off the DPCMA axis.

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses the ESD O-atom source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal O flux and re-examined without air exposure after total exposure times of 2 hrs, 24 hrs, and 63 hrs. The approximate normal distance between the sample face and source in this study was 15 cm, at which distance the flux was about 2.0×10^{13} atoms/cm²-s for the instrument settings used. The sample was maintained at room temperature during the atom exposures with a slight

temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chrome-alumel thermocouple. After the 63-hr AO exposure, the sample was exposed to air (room temperature, ~22°C, relative humidity ~60%) for 4 hrs and again examined using XPS.

3. RESULTS AND DISCUSSION

XPS survey spectra obtained from an as-received, solvent-wiped 20 wt% POSS-polyurethane surface before and after the 2-, 24- and 63-hr O-atom exposure are shown in Figures 4a to 4d, respectively. Spectrum e in Figure 3 was taken after the 4 hr air exposure following the 63 hr O-atom treatment. The peak assignments shown in Figure 4 pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1s, O 1s, Si 2p, Si 2s, O 2s, N 1s, Sn 3d and the Na and O Auger peaks. The presence of Sn is due to the catalyst system (Dibutyltindilaurate) used during polymer synthesis. Na is present in parts per million levels in the reactants used to make the catalyst system and migrates to the surface as a result of AO exposure and affinity for silica. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. Estimates of the near-surface compositions have been calculated from the peak areas in the survey spectra using published atomic sensitivity factors (31) with the assumption of a laterally homogeneous surface. The compositions determined in this manner are presented in Table 1 for the as-entered, O-exposed and air exposed surfaces.

Table 1 Near-surface composition determined from XPS data obtained from the as-entered, solvent cleaned, O-atom and air-exposed 20 wt % POSS-Polyurethane sample

| Surface Sample Treatment | AO Fluence, O/cm ² | O | Si | Composition, at% | | | | Atom ratio O/Si |
|--|----------------------------------|------|------|------------------|-----|------|-----|--------------------|
| | | | | C | Sn | Na | N | |
| As entered, solvent cleaned | — | 18.5 | 8.1 | 72.5 | 0.9 | - | - | 2.28 |
| 2-h O-atom exposure | 1.44×10^{17} | 20.4 | 7.9 | 70.7 | 1.0 | - | - | 2.58 |
| 24-h O-atom exposure | 1.77×10^{18} | 21.8 | 9.5 | 61.7 | 1.0 | 3.0 | 3.0 | 2.29 |
| 63-h O-atom exposure | 4.53×10^{18} | 32.6 | 11.1 | 37.8 | 1.8 | 13.6 | 3.1 | 2.93 |
| 4.0-h air exposure following 63-h O-atom exposure | 4.53×10^{18} | 38.9 | 13.7 | 43.4 | 2.0 | 2.0 | - | 2.83 |

XPS probes the near-surface region of the sample and yields a weighted average composition, with the atomic layers near the surface being weighted more heavily since these photoemitted electrons have a lower probability of scattering inelastically. The sampling depth is ~30 atomic layers, and ~10% of the signal originates from the outermost atomic layer (32). This near-surface region is nonhomogeneous because the AO reacts with the outermost few atomic layers. Therefore, the region that is affected to the greatest extent as a result of the reaction with AO also makes the largest contribution to the XPS signal. This fact implies that XPS is an excellent technique for studying AO erosion of spacecraft materials. Even though the distribution functions involving the depth of chemical reactions in the near-surface region and the XPS determination of the weighted average composition of the near-surface region are complex, the compositional values provide a trend which is indicative of the chemical alterations occurring during AO exposure. The compositions determined using the homogeneous assumption and are shown in Table 1 as a function of AO fluence.

The O 1s-to-Si 2p atomic ratio is 2.28 for the as-entered sample; increases to 2.58, decreases to 2.29 and again increases to 2.93 after the 2, 24 and 63 hr O-atom exposures,

respectively. After the 4-hr air exposure, the O 1s-to-Si 2p atomic ratio slightly decreases to 2.83. However, the overall increase in the O 1s-to-Si 2p atomic ratio resulting from exposure to the O-atom flux is a trend that has previously been observed in two other similar studies of a POSS-PDMS (polydimethylsiloxane) and 60 wt% POSS-PU copolymer. (25,26) It is attributed to the formation of SiO_2 and is consistent with the high-resolution spectra that follow. A significant reduction in the C 1s peak is observed as a result of the incremental exposures to the O-atom flux. The near-surface C concentration decreases from 72.5 at% for the as-entered sample to 37.8 at% after the 63-hr exposure. This decrease in C is due to the reaction of C in the near-surface region with O to form CO_2 . A slight increase in the carbon contribution to 43.4 at% is observed after exposing to air for 4 hrs, probably due to the adsorption of C-containing molecules from the air. Hydrogen in the POSS would also react with the AO to form water which would desorb.

High-resolution XPS C 1s, O 1s and Si 2p obtained from the as-received, solvent-wiped surface before and after the 2-, 24- and 63-hr O-atom exposures are shown in Spectra a-d of Figures 5, 6 and 7, respectively. Spectrum e was obtained after the 4-hr air exposure following the 63-hr O-atom exposure. Variations in peak shapes and positions are observed between the nonexposed, O-atom-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the O-atom flux and then to air.

The C 1s peak, shown in Figure 5a, is broad and centered at 285 eV, indicating that the predominant form of carbon present for the as-entered sample is aliphatic, located on the hard and soft segments of the polymer chain and the cyclopentyl groups on the POSS cages. (33) In Spectra b-d, the C 1s peak becomes broader, displaying visible shoulders with increasing exposure to the O-atom flux. A shoulder due to aromatic carbon is present in these spectra at

284.7 eV. Shoulders are also visible on the high BE side of the C 1s peak in Spectra b, c and d. These probably are due to species such as alcohols, formaldehydes (BE ~286.0 to 287.7 eV) and organic acids (BE ~287.5) which form by reaction with the O-atom flux. These changes coincide with a decrease in the total carbon concentration in the near surface region from 72.5 to 37.8 at%. Dramatic reductions in the carbon concentrations after AO exposure were also seen in the POSS-PDMS and 60 wt% POSS-PU samples studied previously and suggested the selective removal of the cyclohexyl or cyclopentyl groups surrounding the POSS cages. Exposure to air (spectrum e) results in a 5.6 at% increase in C. The O-atom exposure generates reactive surface sites which apparently adsorb hydrocarbons from the air.

The O 1s spectra obtained from the as-entered sample is shown in Figure 6 (Spectrum a). This peak is broad and centered at 532.1 eV. The predominant form of oxygen present for the as-entered sample corresponds to the carbonyl in the urethane segment (531.9 eV) of the polymer and the oxygen present in the POSS cages (532.0 eV). The oxygen content on the surface gradually increases with increasing exposures to the oxygen atom source. After 63-hr total exposure the oxygen content increases from an initial 18.5 to 32.6 at%. This increase coincides with the O 1s spectra in b c and d shifting to a higher binding energy corresponding to the formation of silica on the surface. This trend was also observed and reported in the two previous studies on the POSS-PDMS and a 60 wt% POSS-PU copolymers. Na also migrates to the surface from the bulk of the polymer as the silica layer is being formed. After 63 hrs the Na concentration is 13.6 at%. Exposure to air results in a 6.3 at% increases in the surface O content as the reactive surface adsorbs hydrocarbons from the air, changing the relative composition on the surface of the polymer. However, the peak remains centered at the binding energy

corresponding to SiO_2 , thus indicating that the silica layer formed is chemically stable. This conclusion is corroborated by the Si 2p spectra discussed next.

The Si 2p peaks obtained from the sample after the various treatments are shown in Figure 7. The Si 2p peak for the as-entered sample Spectrum a) is broad, indicating the presence of several chemical states of silicon. This peak is centered at a BE of 102.7 eV, which corresponds to $\text{RSiO}_{1.5}$ in the POSS cage. However, Spectra b, c and d reveal the formation of a SiO_2 layer with incremental exposures to the O-atom flux. The fact that little difference is observed in the spectra obtained after the 24-hr and 63-hr exposures indicates that this silica layer forms a protective barrier on the surface, which prevents further degradation of the polymer with longer exposure to the O-atom flux. The 5-eV AO is not energetic enough to penetrate more than one or two atomic layers into the polymer, while XPS probes as deeply as 30 or more atomic layers beneath the surface. The significant compositional changes observed indicate that most of the near-surface region examined by XPS is altered by the AO exposure. The chemical reactions which form CO_2 and H_2O are exothermic, so the local surface temperature may be relatively high. This and the fact that the AO induces a chemically induced driving force result in diffusion of subsurface C and H to the surface where they react with the AO. This mechanism is responsible for the subsurface compositional alterations observed using XPS.

4. CONCLUSION

The surface of a film of a polyhedral oligomeric silsesquioxane-polyurethane copolymer has been characterized in-situ using XPS before and after exposure to different fluences of oxygen atoms produced by an ESD hyperthermal oxygen atom source. The XPS data indicate that exposure to AO reduces the carbon content on the surface from 72.5 to 37.8 at% after a 63-

hr exposure to an AO flux of 10^{13} atoms/cm²-s. The oxygen and silicon concentrations in the near-surface region determined using XPS increase with increasing exposure to the AO flux. The oxygen-to-silicon ratio increases from 2.28 for the as-entered sample to 2.93. High resolution XPS data suggests that the atomic oxygen initially attacks the cyclopentyl groups on the POSS cage, forming CO₂ and water, which desorb. Increased exposure to the O-atom flux results in the formation of a silica layer on the surface, which acts as a protective barrier preventing further degradation of the underlying polymer. Exposure to air results in the adsorption of hydrocarbon species on the surface.

FIGURE CAPTIONS

- Figure 1** POSS-polymer structures.
- Figure 2** Schematic Diagram of the Atomic Oxygen Source.
- Figure 3** Synthetic scheme for synthesis of POSS-polyurethane.
- Figure 4** XPS survey spectra obtained from a solvent-cleaned, 20-wt% POSS-Polyurethane film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.0 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 5** XPS C 1s spectra obtained from a solvent-cleaned, 20-wt% POSS-Polyurethane film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.0 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 6** XPS O 1s spectra obtained from a solvent-cleaned, 20-wt% POSS-Polyurethane film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.0 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 7** XPS Si 2p spectra obtained from a solvent-cleaned, 20-wt% POSS-Polyurethane film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.0 hr air exposure following the 63 hr O-atom exposure (e).



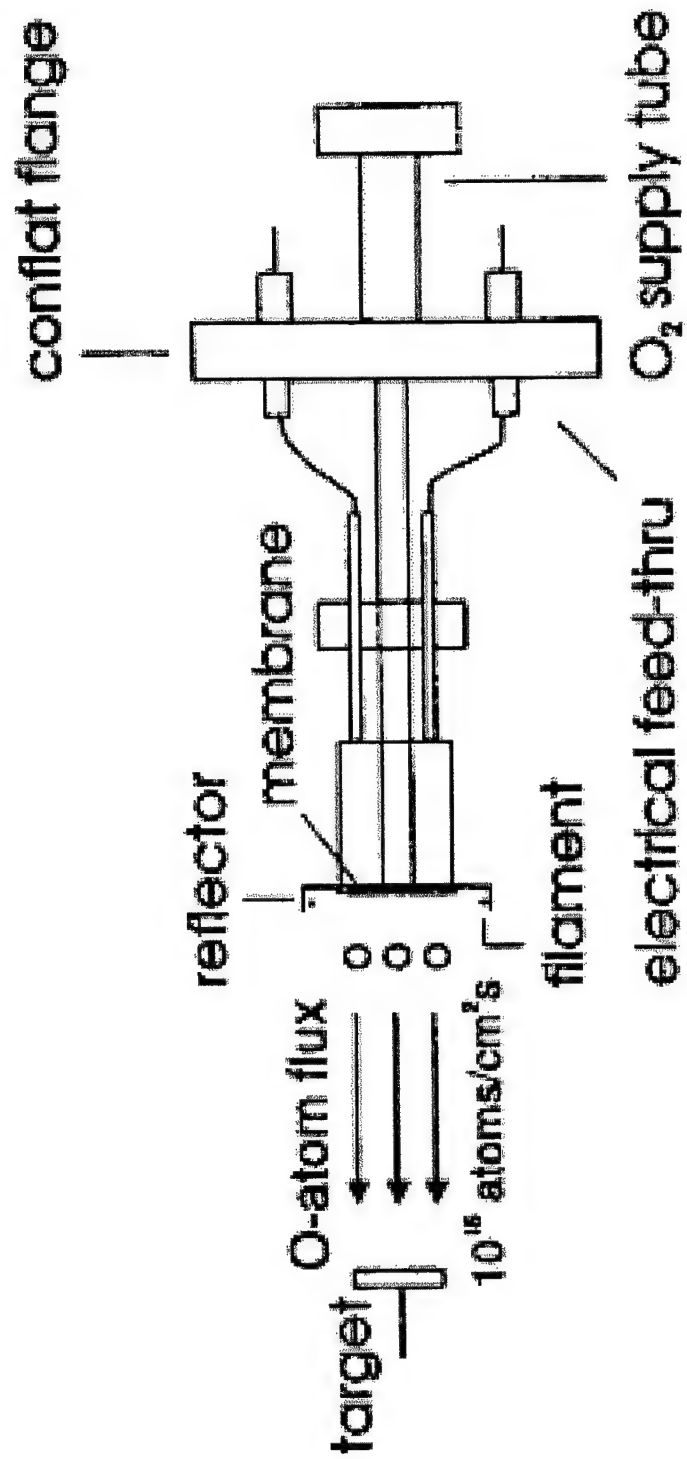
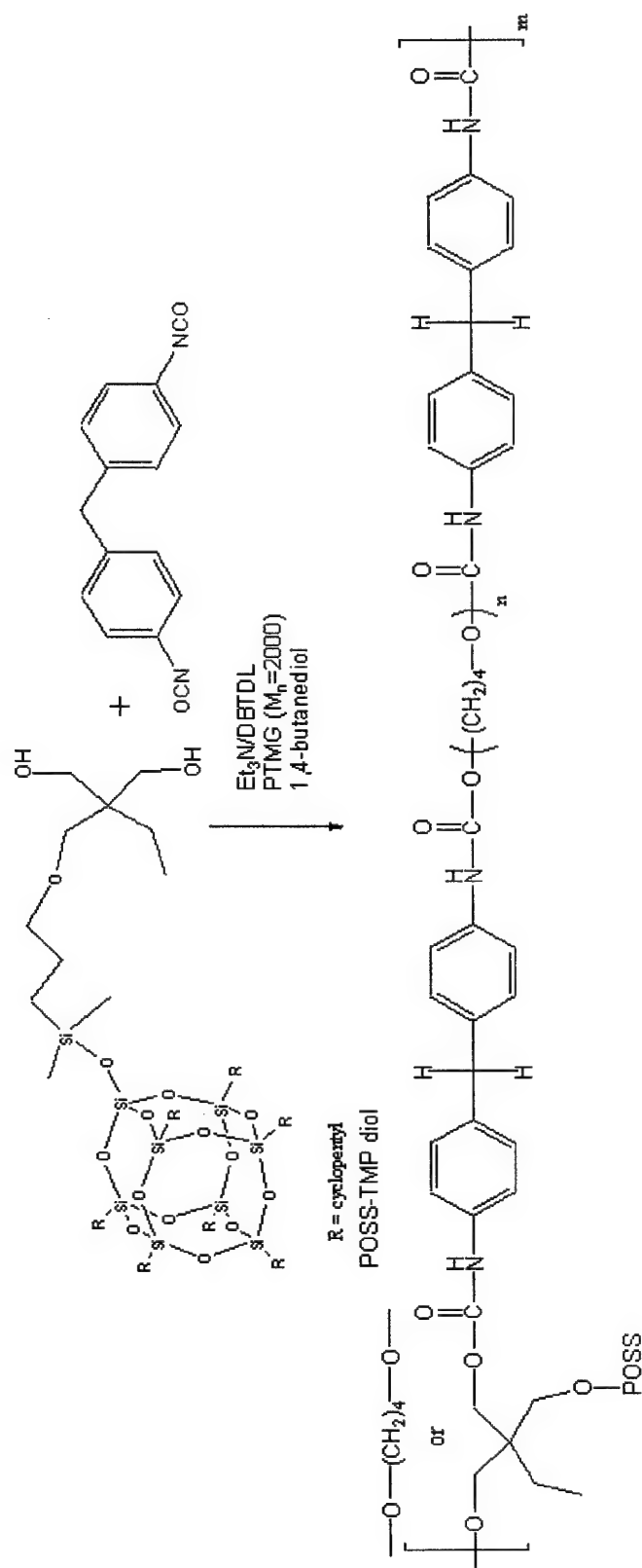


Figure 2.

Figure 3.



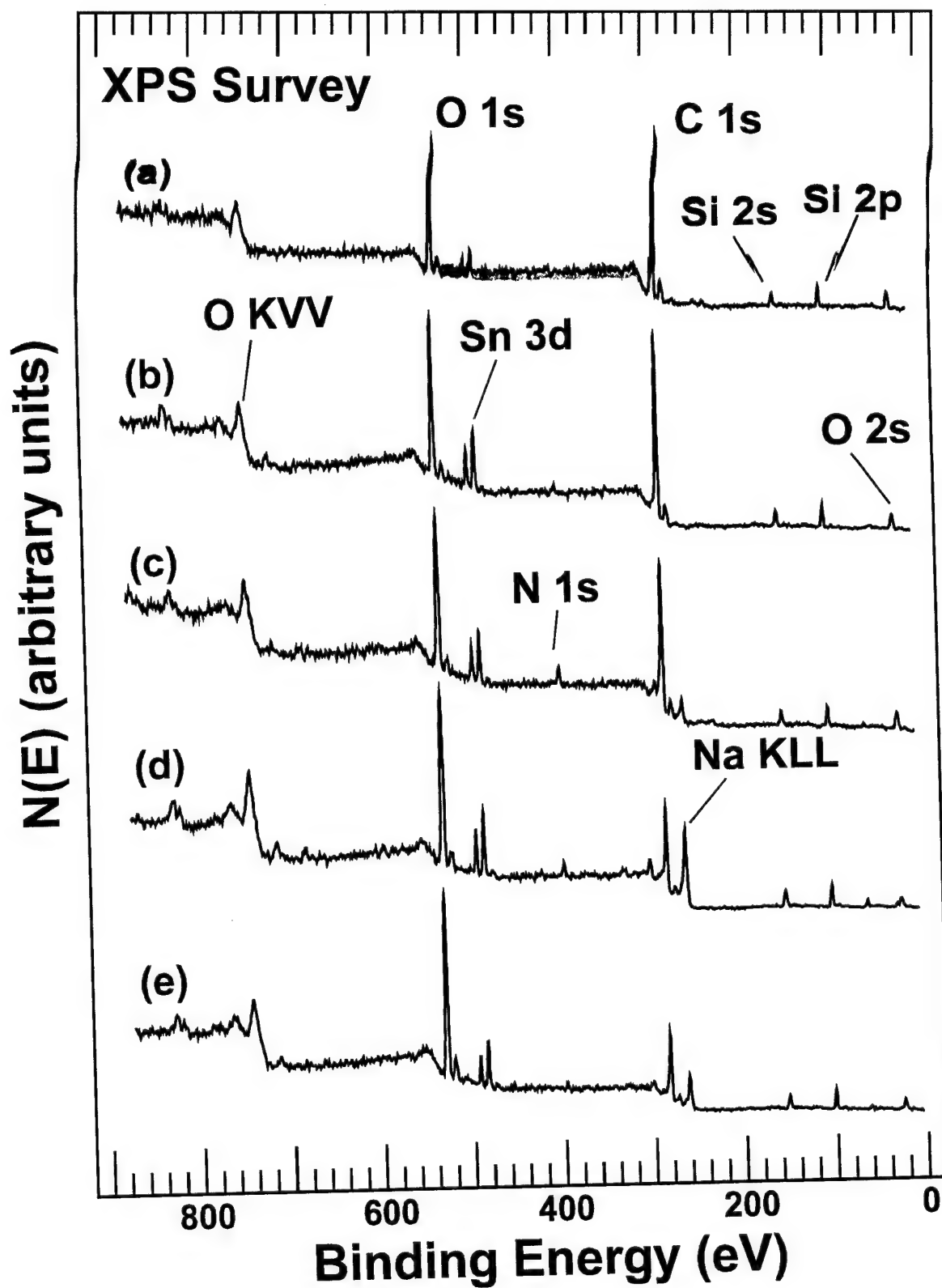


Figure 4.

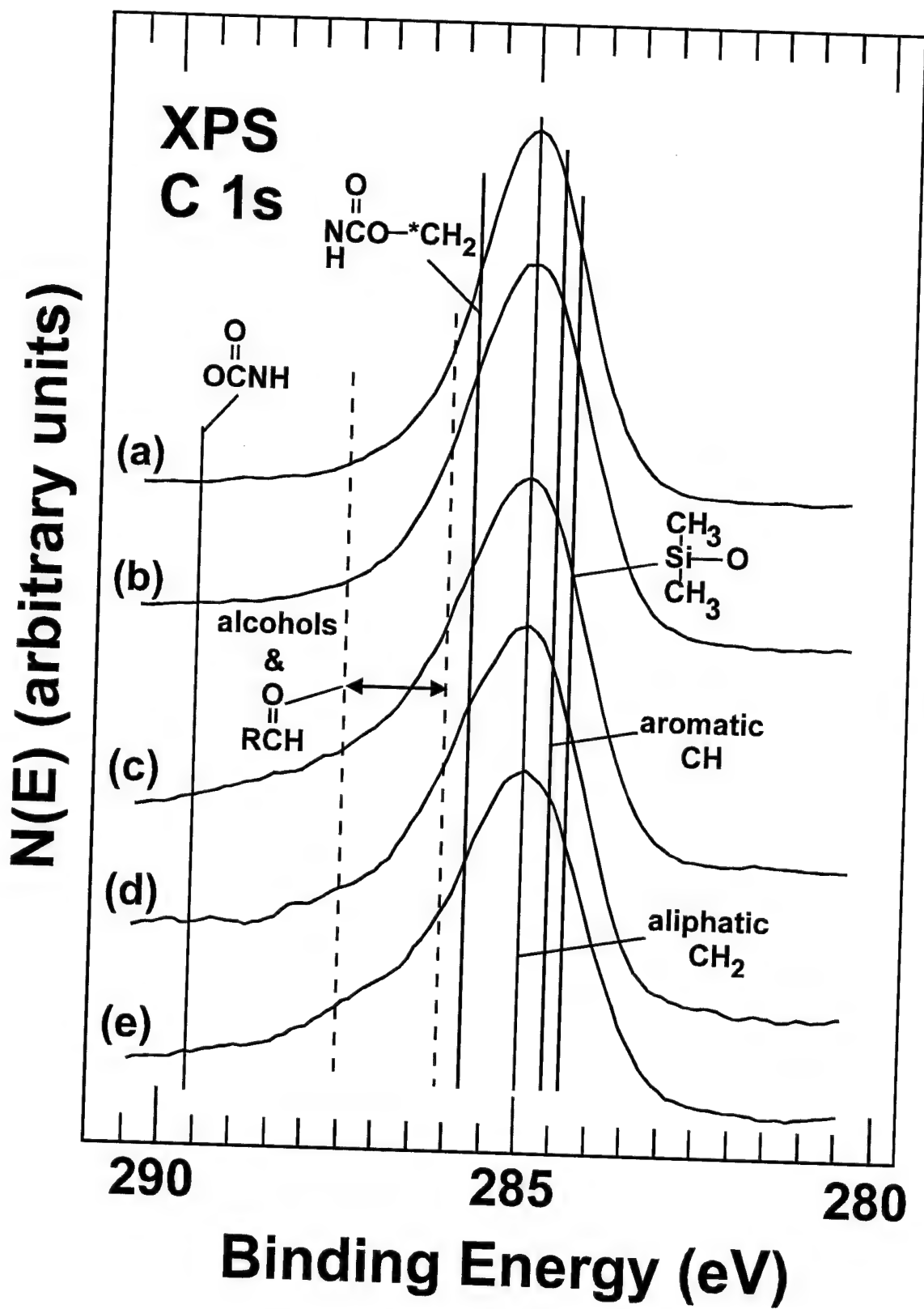


Figure 5.

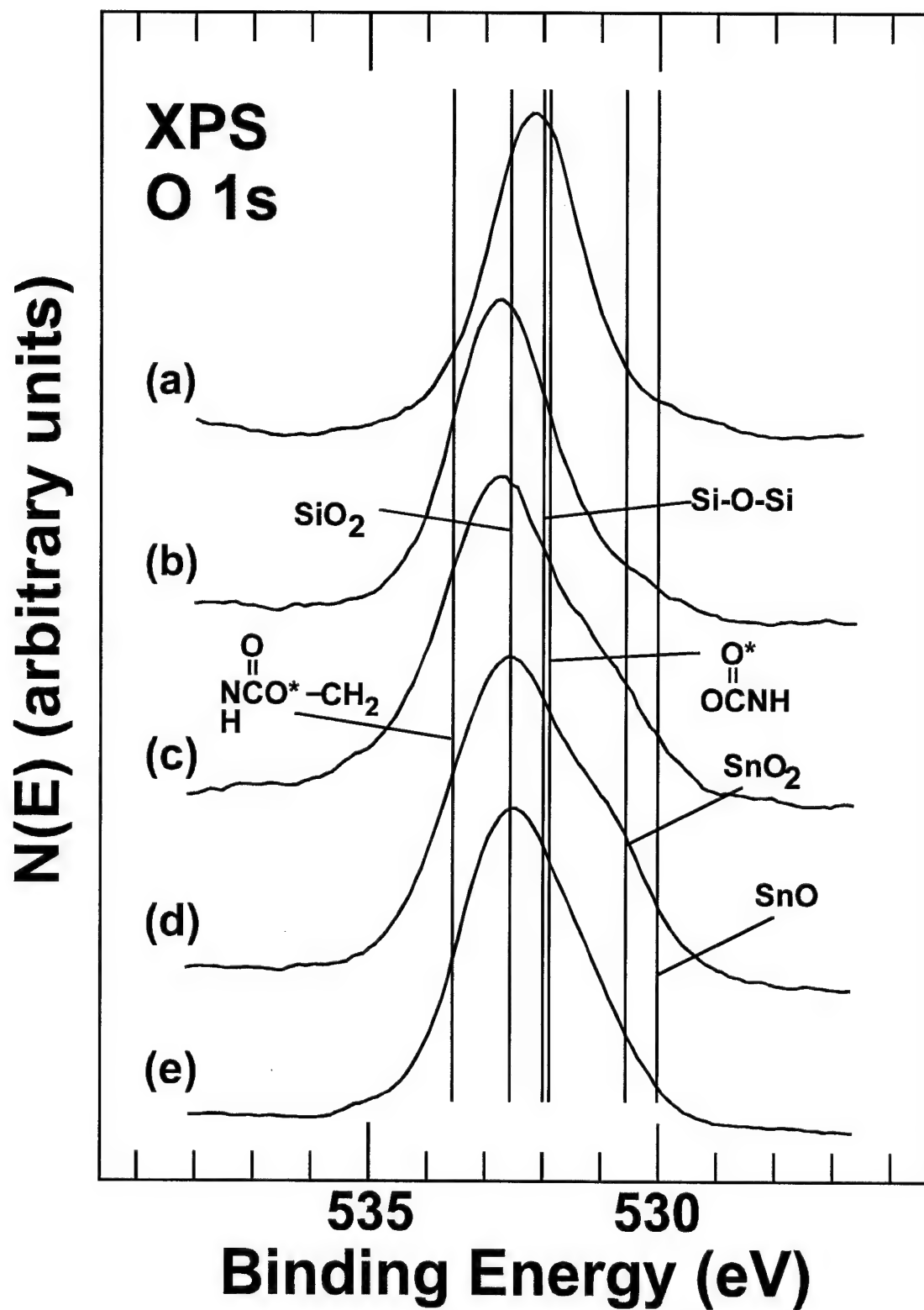


Figure 6.

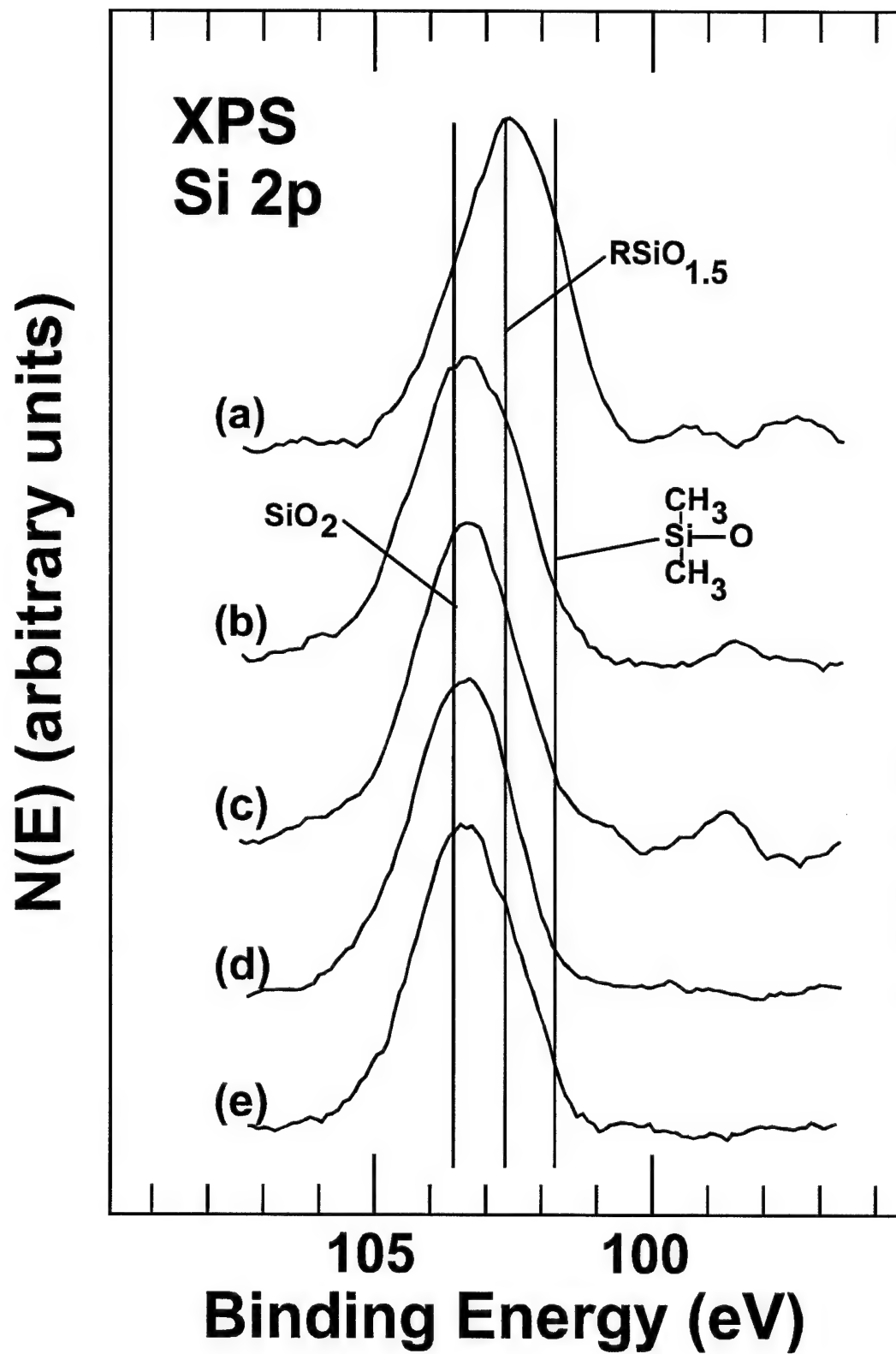


Figure 7.

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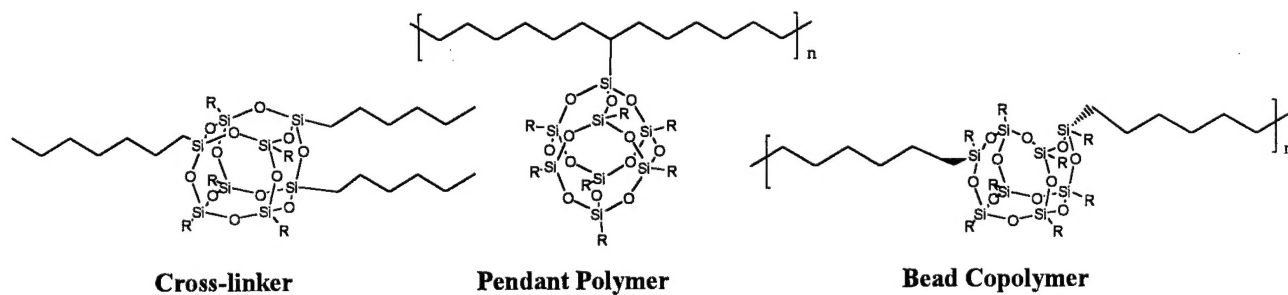


Figure 1.

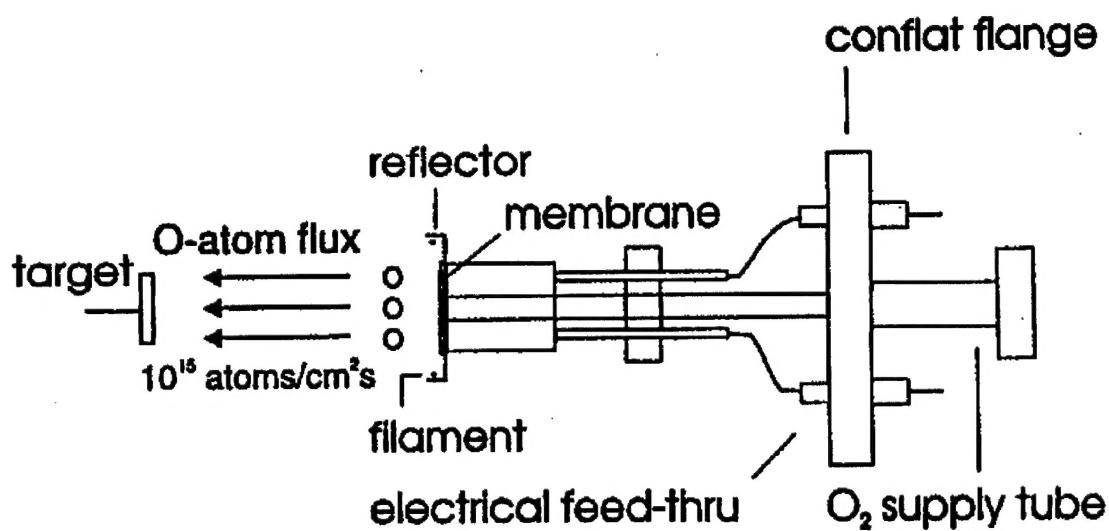


Figure 2.

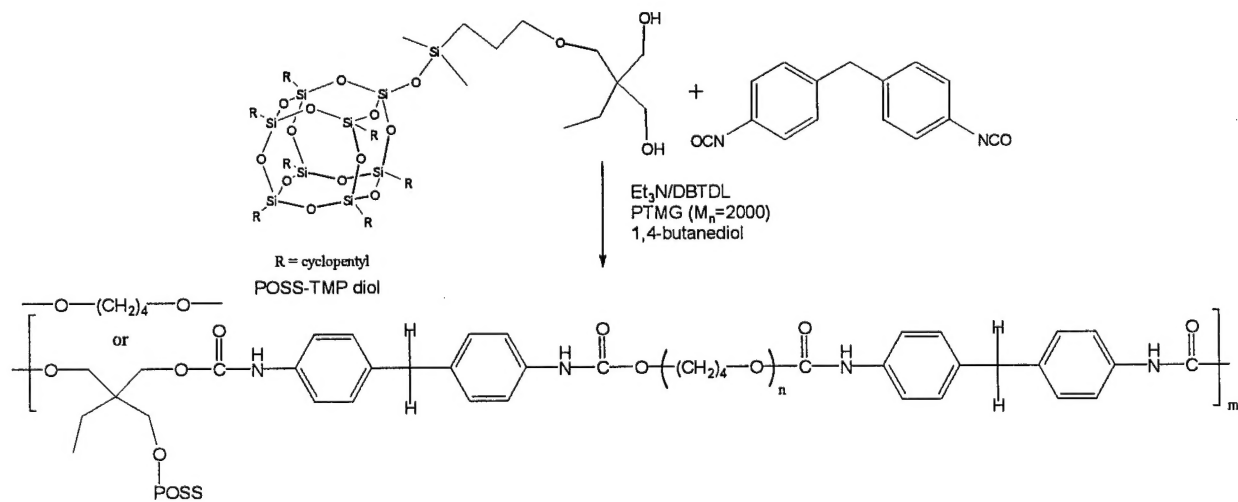


Figure 3.